

## PATENT ABSTRACTS OF JAPAN

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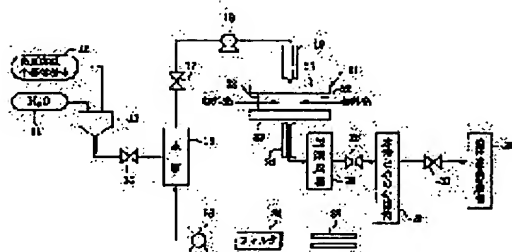
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## (54) PRODUCTION OF HYDROGEN GAS

## (57)Abstract:

PROBLEM TO BE SOLVED: To easily produce high-pressure hydrogen gas with high reaction efficiency without loss of a catalyst due to the dissolution in a liq. reactant.

SOLUTION: The powder 12 of a photoreactive semiconductor is uniformly dispersed in water 11 to prepare a dispersion. The dispersion is made subcritical or supercritical and then irradiated with light to decompose the water into hydrogen gas and oxygen gas. The oxygen gas is removed from the subcritical or supercritical water contg. the produced hydrogen gas and oxygen gas and the powder 12. The temp. pressure or both of the subcritical or supercritical remainder freed from the oxygen gas are lowered to liberate high-pressure hydrogen gas.



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CLAIMS

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[Claim(s)]

[Claim 1] The process which makes the dispersion liquid which distributed photoreaction nature semi-conductor powder (12) to homogeneity in water (11), The process which changes said dispersion liquid into a subcritical state or a supercritical condition, and irradiates light at said dispersion liquid, and disassembles said water (11) into hydrogen gas and oxygen gas, The process which removes oxygen gas from the water (11) containing said powder (12) of the subcritical state decomposed into said hydrogen gas and oxygen gas, or a supercritical condition, The manufacture approach of hydrogen gas including the process which takes out high-pressure hydrogen gas by reducing either or the both sides of the pressure of the remainder of the subcritical state which removed said oxygen gas, or a supercritical condition, or temperature.

[Claim 2] They are remaining as it is or the manufacture approach of hydrogen gas according to claim 1 which is filtered and is added to dispersion liquid about drawing and the cooled residual liquor in high-pressure hydrogen gas.

[Claim 3] The process which supplies water (41) to the 1st room (53) which is divided with the separator (52) on which the photoreaction nature semi-conductor metal plate (49) and the metal plate (51) which supports this were stuck, and faces said semi-conductor metal plate (49), and the 2nd room (54) which faces said support metal plate, respectively, The process which disassembles said water of the 1st room (53) into oxygen gas, and disassembles said water of the 2nd room (54) into hydrogen gas, respectively by changing said water of the 1st room (53) and the 2nd room (54) into a subcritical state or a supercritical condition, respectively, and irradiating light at said semi-conductor metal plate (49), The manufacture approach of hydrogen gas including the process which takes out high-pressure hydrogen gas by reducing either or the both sides of the pressure of the water containing the hydrogen gas of the subcritical state produced in said 2nd room (54), or a supercritical condition, or temperature.

[Claim 4] The manufacture approach of hydrogen gas according to claim 3 of adding this residual liquor to the water (41) supplied to the 1st room (53) and the 2nd room (54) after cooling the residual liquor which took out high-pressure hydrogen gas.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the approach of irradiating light, photodissociating it in the water which the photoreaction nature semi-conductor powder of a subcritical state or a supercritical condition distributed, and manufacturing high-pressure hydrogen gas.

[0002]

[Description of the Prior Art] Conventionally light is irradiated at the water which contains the photoreaction nature semi-conductor of TiO<sub>2</sub>, ZrO<sub>2</sub>, SrTiO<sub>3</sub>, and K<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> grade as a catalyst under ordinary temperature ordinary pressure, water is photodissociated, and the method of generating hydrogen gas on a catalyst front face is learned (for example, JP, 7-88380, A, this 9-70533, this 9-142804, this 10-1301).

[0003]

[Problem(s) to be Solved by the Invention] however, by the above-mentioned conventional approach performed under ordinary temperature ordinary pressure \*\* Since the air bubbles of hydrogen gas are generated in the reaction mixture which hydrogen gas adheres to a catalyst front face, and reaction effectiveness falls, and contains \*\* catalyst and water, Since the phenomenon of the optical dissolution which a catalyst dissolves into reaction mixture when light is scattered about within reaction mixture, the permeability of exposure light worsens and light hits \*\* catalyst arises, In are necessary to supply a continuously new catalyst and manufacturing the hydrogen gas of \*\* high pressure, there are problems, like there is the need of pressurizing the generated hydrogen gas. The purpose of this invention is to offer the manufacture approach of hydrogen gas that a catalyst dissolves in reaction mixture, it does not lose, and high-pressure hydrogen gas can be easily manufactured at high reaction effectiveness.

[0004]

[Means for Solving the Problem] The process from which invention concerning claim 1 makes the dispersion liquid which distributed the photoreaction nature semi-conductor powder 12 to homogeneity in water 11 as shown in drawing 1 , The process which changes the above-mentioned dispersion liquid into a subcritical state or a supercritical condition, and irradiates light at the above-mentioned dispersion liquid, and disassembles water 11 into hydrogen gas and oxygen gas, The process which removes oxygen gas from the water 11 containing the semi-conductor powder 12 of the subcritical state decomposed into the above-mentioned hydrogen gas and oxygen gas, or a supercritical condition, It is the manufacture approach of hydrogen gas including the process which takes out high-pressure hydrogen gas by reducing either or the both sides of the pressure of the remainder of the subcritical state which removed the above-mentioned oxygen gas, or a supercritical condition, or temperature. Since the water 11 of a subcritical state or a supercritical condition has the outstanding diffusing capacity, the hydrogen gas generated on the front face of the photoreaction nature semi-conductor powder 12 which acts as a catalyst forms water and a homogeneity phase promptly. Consequently, adsorption of the hydrogen gas on the front face of a catalyst decreases, and hydrogen generation effectiveness increases. Moreover, in underwater [ of a subcritical state or a supercritical

condition ], since the solubility of the inorganic ion produced from a catalyst is very low, the phenomenon of the optical dissolution which a catalyst dissolves and loses in reaction mixture cannot happen very easily, and the deployment of a catalyst of it is attained. Moreover, high-pressure hydrogen gas is obtained, without establishing a special pressurization means. Invention concerning claim 2 is invention concerning claim 1, and as shown in drawing 1 , it is remaining as it is or the manufacture approach of hydrogen gas which is filtered and is added to dispersion liquid about drawing and the cooled residual liquor in high-pressure hydrogen gas. The residual liquor which took out high-pressure hydrogen gas is reused as a part of dispersion liquid.

[0005] The process which invention concerning claim 3 is divided with the separator 52 on which the photoreaction nature semi-conductor metal plate 49 and the metal plate 51 which supports this were stuck as shown in drawing 4 , and faces the semi-conductor metal plate 49, which faces 53 and the support metal plate 51 the 1st room and which supplies the 2nd room of water 41 to 54, respectively. The process which disassembles the water 41 of 53 into oxygen gas, and disassembles the 1st room of the 1st room of the 2nd room of the water 41 of 54 into hydrogen gas, respectively 53 and by changing the 2nd room of the water 41 of 54 into a subcritical state or a supercritical condition, respectively, and irradiating light at the semi-conductor metal plate 49. It is the manufacture approach of hydrogen gas including the process which takes out high-pressure hydrogen gas by reducing either or the both sides of the pressure of the water 41 containing the hydrogen gas of the subcritical state produced in 54 the 2nd room, or a supercritical condition, or temperature. When light is irradiated at the photoreaction nature semi-conductor metal plate 49, water decomposes on the semi-conductor metal plate 49, and it is  $\text{H}_2\text{O} + 2\text{p}^+ \rightarrow 1/2\text{O}_2^{**} + \text{H}^+$  and the 1st room of oxygen gas occurs in 53. Moreover, when light is irradiated at the semi-conductor metal plate 49, water decomposes on the support metal plate 51, and it is  $\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2^{**}$  , and the 2nd room of hydrogen gas is generated in 54. Since the water of a subcritical state or a supercritical condition has the high pressure, the collision frequency of the molecule of water and the support metal plate 51 increases, and hydrogen generation effectiveness increases. Moreover, high-pressure hydrogen gas is obtained, without establishing a special pressurization means. Invention concerning claim 4 is invention concerning claim 3, and as shown in drawing 4 , after it cools the residual liquor which took out high-pressure hydrogen gas, it is the manufacture approach of hydrogen gas of adding the 1st room of this residual liquor to 53 and the water 41 supplied to 54 the 2nd room. The residual liquor which took out high-pressure hydrogen gas is reused as some electrolytic solutions.

[0006]

[Embodiment of the Invention] In this invention, the subcritical state of water means the condition of the water which is 200–374 degrees C in temperature, and is in the pressure of 160–215kg/cm<sup>2</sup>. Moreover, the supercritical condition of water means the condition of the water which is 374–400 degrees C in temperature, and is in the pressure of 215–300kg/cm<sup>2</sup>. A reaction is slow and the decomposition effectiveness of water is not good at under the lower limit of the temperature in a subcritical state, and a pressure. Moreover, if the upper limit of the temperature in a supercritical condition and a pressure is exceeded, a load is applied to a reaction container too much, and this is not efficient, either.

[0007] The manufacture approach of the hydrogen gas concerning claims 1 and 2 of this invention is explained based on drawing 1 – drawing 3 . As shown in drawing 1 , the photoreaction nature semi-conductor powder 12 of water (H<sub>2</sub>O) 11 and a photocatalyst is put into the churning container 13, is agitated, and the dispersion liquid (reaction mixture) which distributed the photoreaction nature semi-conductor powder 12 in water 11 at homogeneity are prepared. The photoreaction nature semi-conductor powder 12 is a particle whose particle size of the structure where metallic oxides, such as titanium oxide, a zinc oxide, tungstic oxide, and cerium oxide, the compound metallic oxide of the Rb-Nb and Pb-Nb systems, etc. were supported on metals, such as a zirconium, platinum, and nickel, is 10–500 micrometers. The above-mentioned dispersion liquid are supplied to a tank 16 through a bulb 14. The dispersion liquid stored in this tank 16 are pressurized with a pump 18 through a bulb 17, and are heated by the pre-heater 19, will be in a subcritical state or a supercritical condition, and will be fed by the

reaction container 21. The aperture 22 which consists of ingredients which make the exposure light shown in the reaction container 21 by the arrow head of drawing 1 penetrate, such as sapphire and a diamond, is formed. Although ultraviolet rays with a wavelength of 300nm or less are desirable as an exposure light, the light which has the wavelength beyond this can also be used. A mercury lamp, a halogen lamp, etc. are used as such a source of an optical exposure. The heater 23 which heats the reaction container 21 is formed in vertical both sides of the reaction container 21, and, as for dispersion liquid, this maintains a subcritical state or a supercritical condition in the reaction container 21.

[0008] If light is irradiated from an aperture 22 in this condition at the dispersion liquid in the reaction container 21, light will decompose a water molecule in the front face of the photoreaction nature semi-conductor powder 12 of a photocatalyst, and as shown in a degree type, it will produce hydrogen gas and oxygen gas.

$2H_2O \rightarrow 2H_2 + O_2$  After the dispersion liquid containing the hydrogen gas and oxygen gas which occurred with  $O_2$  reaction container 21 are taken out from the reaction container 21 and heated by predetermined temperature at a heater 24, they are sent to the deoxidation tub 26. In response to as shown in drawing 2, while maintaining many predetermined spacing, and being arranged so that touch area with the as sufficient plate 27 of metals, such as oxygen and titanium which reacts, as dispersion liquid can be secured to the wall of the deoxidation tub 26, consequently dispersion liquid's passing through the inside of the deoxidation tub 26, the oxygen in dispersion liquid is removed for a metal plate 27 and oxygen. The dispersion liquid which are removed in oxygen and contain hydrogen gas are taken out from the deoxidation tub 26, and are divided into water and high-pressure hydrogen gas by being sent to the separation tub 29 of hydrogen and water through a bulb 28, and descending a pressure.

[0009] The separated high-pressure hydrogen gas is sent and saved through a bulb 31 at the high-pressure hydrogen storage tank 32. The residual liquor which took out hydrogen and the high-pressure hydrogen gas by the separation tub 29 of water from dispersion liquid is sent to a filter 34, after being cooled with a condensator 33. Since the photoreaction nature semi-conductor powder 12 contained in residual liquor is the particle of structure which made metallic oxides, such as titanium oxide, support on metals, such as a zirconium and platinum, as mentioned above, after being used as a photocatalyst within the reaction container 21, the platinum of a support metal and the titanium oxide of a metallic oxide may dissociate, for example, and it may lose the function as a photocatalyst. In such a case, the support metal and metallic oxide which were separated are filtered and removed with the above-mentioned filter 34. The residual liquor which passed the filter 34 is pressurized with a pump 36, is collected by the tank 16, and is reused as a part of dispersion liquid sent to the reaction container 21. When the photoreaction nature semi-conductor powder 12 has not lost the function as a photocatalyst, after being cooled with a condensator 33, directly, it is sent to a pump 36 and the residual liquor which took out hydrogen and the high-pressure hydrogen gas by the separation tub 29 of water from dispersion liquid is pressurized without sending to a filter 34, it is collected by the tank 16, and is reused as a part of dispersion liquid sent to the reaction container 21.

[0010] In the embodiment based on drawing 1 and drawing 2, the deoxidation tub 26 is formed independently in the outside of the reaction container 21. However, it is also possible to form the deoxidation tub 26 inside the reaction container 21 at the reaction container 21 and one besides this. For example, as shown in drawing 3, deactivator 37 may be formed in the outlet part in the reaction container 21, and the oxygen produced within the reaction container 21 may be removed. That is, many predetermined spacing is maintained and it is arranged at the wall of deactivator 37 so that oxygen and touch area with the as sufficient metal plate 38 which reacts as dispersion liquid can be secured, and in response to as an arrow head shows, while the dispersion liquid containing the hydrogen gas and oxygen gas which occurred with the reaction container 21 pass through the inside of deactivator 37, the oxygen in dispersion liquid is removed for a metal plate 38 and oxygen. Titanium etc. is mentioned as the quality of the material of this metal plate 38. The dispersion liquid which are removed in oxygen and contain hydrogen gas are taken out as an arrow head shows from the outlet of deactivator 37, and they are sent to the separation tub 29 of hydrogen and water through a bulb 28.

[0011] The manufacture approach of the hydrogen gas concerning claims 3 and 4 of this invention is explained based on drawing 4. As shown in drawing 4, water (H<sub>2</sub>O) 41 is supplied to a tank 43 through a bulb 42. The water 41 stored in the tank 43 is pressurized with a pump 46 through a bulb 44, and is heated by the pre-heater 47, will be in a subcritical state or a supercritical condition, and will be fed by the reaction container 48. The reaction container 48 is divided with the separator 52 on which the photoreaction nature semi-conductor metal plate 49 and the metal plate 51 which supports this were stuck. consequently, the photoreaction nature semi-conductor metal plate 49 is faced -- the 1st room faces 53 and the above-mentioned support metal plate 51 -- 54 [ room / 2nd ] is formed. As an ingredient of the photoreaction nature semi-conductor metal plate 49, semi-conductor metals, such as Ti compounds, such as titanium, SrTiO<sub>2</sub>, and BaTiO<sub>4</sub>, and a compound of Nb system, are mentioned. Moreover, metals, such as platinum, a zirconium, nickel, and a rhodium, are mentioned as an ingredient of the support metal plate 51. the water 41 which changed into the subcritical state or the supercritical condition, and was fed by the reaction container 48 -- the reaction container 48 -- the 1st room is supplied to 54 the 2nd room with 53, respectively. the heater 56 which heats the reaction container 48 prepares in vertical both sides of the reaction container 48 -- having -- thereby -- the reaction container 48 -- water maintains the 1st room of a subcritical state or a supercritical condition in 53 and 2nd room 54. The aperture 57 which consists of ingredients, such as sapphire and a diamond, is formed in the reaction container 48.

[0012] In this condition, if ultraviolet rays with a wavelength of 300nm or less are irradiated on the front face of the photoreaction nature semi-conductor metal plate 49 from an aperture 57 as an exposure light, a water molecule will be decomposed in the front face of the semi-conductor metal plate 49, the 1st room of oxygen gas will occur in 53, and hydrogen gas will generate the 2nd room of light in 54. Since 54 [ room / 2nd ] is divided with the separator 52 with 53, the 1st room of the oxygen gas and hydrogen gas which were generated are not mixed. The 2nd room of the water containing the hydrogen gas generated in 54 the 2nd room is taken out from 54, and it is divided into water and high-pressure hydrogen gas by being sent to the separation tub 59 of hydrogen and water through a reducing valve 58, and descending a pressure. The separated high-pressure hydrogen gas is sent and saved through a bulb 61 at the high-pressure hydrogen storage tank 62. After being cooled with a condensator 63, the water separated from hydrogen gas by the separation tub 59 of hydrogen and water is pressurized with a pump 64, is collected by the tank 43, and is reused as some water sent to the reaction container 48. The 1st room of the water containing the oxygen gas which occurred in 53 the 1st room is taken out from 53, and it is divided into water and oxygen gas by being sent to the separation tub 66 of oxygen and water, and descending a pressure. The separated oxygen gas is sent and saved through a bulb 67 at the hyperbaric oxygen storage tank 68. After being cooled with a condensator 69, the water separated from oxygen gas by the separation tub 66 of oxygen and water is collected by the tank 43, and is reused as some water sent to the reaction container 48.

[0013]

[Effect of the Invention] As stated above, according to this invention, the dispersion liquid which distributed photoreaction nature semi-conductor powder to homogeneity are made in water. Change these dispersion liquid into a subcritical state or a supercritical condition, irradiate light, and water is disassembled into hydrogen gas and oxygen gas. Oxygen gas is removed from the water containing the photoreaction nature semi-conductor powder of the subcritical state decomposed into hydrogen gas and oxygen gas, or a supercritical condition. Since high-pressure hydrogen gas was taken out by reducing either or the both sides of the pressure of the remainder of the subcritical state which removed oxygen gas, or a supercritical condition, or temperature The hydrogen gas generated on the front face of the photoreaction nature semi-conductor powder which acts as a catalyst forms water and a homogeneity phase promptly, adsorption of the hydrogen gas on the front face of a catalyst decreases, and hydrogen generation effectiveness increases. Moreover, the phenomenon of the optical dissolution which a catalyst dissolves and loses in reaction mixture cannot happen very easily, and the deployment of a catalyst of it is attained.

[0014] Moreover, according to this invention, it is divided with the separator on which the photoreaction nature semi-conductor metal plate and the metal plate which supports this were stuck. Water is supplied to the 1st room which faces a semi-conductor metal plate, and the 2nd room which faces a support metal plate, respectively. By changing the water of the 1st room and the 2nd room into a subcritical state or a supercritical condition, respectively, and irradiating light at a photoreaction nature semi-conductor metal plate, disassemble the water of the 1st room into oxygen gas, and the water of the 2nd room is disassembled into hydrogen gas, respectively. Since high-pressure hydrogen gas was taken out by reducing either or the both sides of the pressure of the water containing the hydrogen gas of the subcritical state produced in the 2nd room, or a supercritical condition, or temperature, the collision frequency of the molecule of water and a support metal plate increases, and hydrogen generation effectiveness increases. Furthermore, high-pressure hydrogen gas is obtained, without establishing a special pressurization means.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] The block diagram of the manufacturing installation of the hydrogen gas of this invention.

[Drawing 2] The block diagram which explains the structure of a deoxidation tub with the equipment of drawing 1 .

[Drawing 3] The block diagram showing the embodiment which formed deactivator in the interior of a reaction container.

[Drawing 4] The block diagram showing another embodiment of the manufacturing installation of the hydrogen gas of this invention.

[Description of Notations]

11 41 Water

12 Photoreaction Nature Semi-conductor Powder

16 43 Tank

21 48 Reaction container

26 Deoxidation Tub

29 59 Separation tub of hydrogen and water

32 62 High-pressure hydrogen storage tank

49 Photoreaction Nature Semi-conductor Metal Plate

51 Metal Plate

66 Separation Tub of Oxygen and Water

68 Hyperbaric Oxygen Storage Tank

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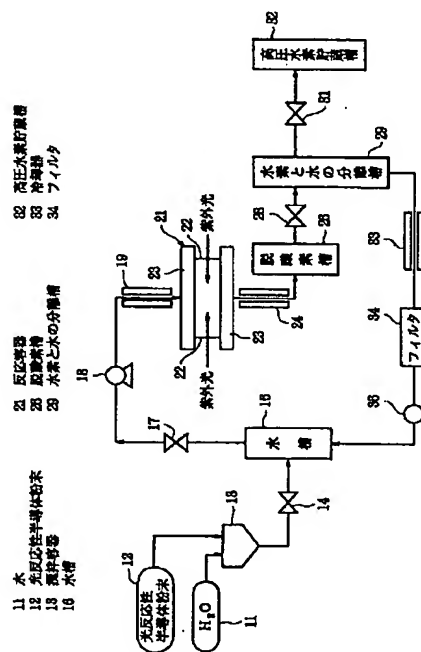
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(54) 【発明の名称】 水素ガスの製造方法

(57) 【要約】

【課題】 触媒が反応液に溶解して喪失することがなく、高い反応効率で容易に高圧の水素ガスを製造する。  
【解決手段】 水11に光反応性半導体粉末12を均一に分散した分散液を作る。この分散液を亜臨界状態又は超臨界状態にして光を照射して水を水素ガスと酸素ガスに分解する。水素ガスと酸素ガスに分解した亜臨界状態又は超臨界状態の半導体粉末12を含む水から酸素ガスを取除く。酸素ガスを取除いた亜臨界状態又は超臨界状態の残部の圧力又は温度のいずれか一方又は双方を低下させることにより高圧の水素ガスを取り出す。



## 【特許請求の範囲】

【請求項 1】 水(11)に光反応性半導体粉末(12)を均一に分散した分散液を作る工程と、

前記分散液を亜臨界状態又は超臨界状態にしかつ前記分散液に光を照射して前記水(11)を水素ガスと酸素ガスに分解する工程と、

前記水素ガスと酸素ガスに分解した亜臨界状態又は超臨界状態の前記粉末(12)を含む水(11)から酸素ガスを取除く工程と、

前記酸素ガスを取除いた亜臨界状態又は超臨界状態の残部の圧力又は温度のいずれか一方又は双方を低下させることにより高圧の水素ガスを取出す工程とを含む水素ガスの製造方法。

【請求項 2】 高圧の水素ガスを取出し、冷却した残液をそのまま或は濾過して、分散液に加える請求項 1 記載の水素ガスの製造方法。

【請求項 3】 光反応性半導体金属板(49)とこれを担持する金属板(51)が貼り合わされた隔離板(52)で仕切られ前記半導体金属板(49)に面する第 1 室(53)と前記担持金属板に面する第 2 室(54)にそれぞれ水(41)を供給する工程と、

前記第 1 室(53)及び第 2 室(54)の水をそれぞれ亜臨界状態又は超臨界状態にしかつ前記半導体金属板(49)に光を照射することにより前記第 1 室(53)の水を酸素ガスに前記第 2 室(54)の水を水素ガスにそれぞれ分解する工程と、

前記第 2 室(54)で生じた亜臨界状態又は超臨界状態の水素ガスとを含む水の圧力又は温度のいずれか一方又は双方を低下させることにより高圧の水素ガスを取出す工程とを含む水素ガスの製造方法。

【請求項 4】 高圧の水素ガスを取出した残液を冷却した後、この残液を第 1 室(53)及び第 2 室(54)に供給する水(41)に加える請求項 3 記載の水素ガスの製造方法。

## 【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は亜臨界状態又は超臨界状態の光反応性半導体粉末が分散した水に光を照射して光分解し高圧水素ガスを製造する方法に関するものである。

【0002】

【従来の技術】従来より、常温常圧の下で  $TiO_2$ 、 $ZrO_2$ 、 $SrTiO_3$ 、 $K_4Nb_6O_{17}$  等の光反応性半導体を触媒として含む水に光を照射して水を光分解し、水素ガスを触媒表面で発生させる方法が知られている(例えば、特開平 7-88380、同 9-70533、同 9-142804、同 10-1301)。

【0003】

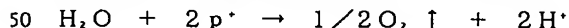
【発明が解決しようとする課題】しかし常温常圧の下で行われる上記従来方法では、①触媒表面に水素ガスが付着して反応効率が低下し、②触媒と水を含む反応液中に

水素ガスの気泡が発生するため、反応液内で光が散乱して照射光の透過性が悪くなり、③触媒に光が当たることにより触媒が反応液中に溶解する光溶解の現象が生じるため、絶えず新しい触媒を補給することが必要となり、また④高圧の水素ガスを製造する場合には、発生した水素ガスを加圧する必要がある等の問題がある。本発明の目的は、触媒が反応液中に溶解して喪失することがなく、高い反応効率で容易に高圧の水素ガスを製造できる水素ガスの製造方法を提供することにある。

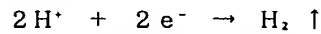
【0004】

【課題を解決するための手段】請求項 1 に係る発明は図 1 に示すように、水 11 に光反応性半導体粉末 12 を均一に分散した分散液を作る工程と、上記分散液を亜臨界状態又は超臨界状態にしかつ上記分散液に光を照射して水 11 を水素ガスと酸素ガスに分解する工程と、上記水素ガスと酸素ガスに分解した亜臨界状態又は超臨界状態の半導体粉末 12 を含む水 11 から酸素ガスを取除く工程と、上記酸素ガスを取除いた亜臨界状態又は超臨界状態の残部の圧力又は温度のいずれか一方又は双方を低下させることにより高圧の水素ガスを取出す工程とを含む水素ガスの製造方法である。亜臨界状態又は超臨界状態の水 11 は優れた拡散能力を有するため、触媒として作用する光反応性半導体粉末 12 の表面で発生した水素ガスは速やかに水と均一相を形成する。この結果、触媒表面への水素ガスの吸着は少なくなり水素生成効率が増大する。また亜臨界状態又は超臨界状態の水中では触媒から生じる無機イオンの溶解度が極めて低いため、触媒が反応液中に溶解して喪失する光溶解の現象が極めて起こり難く、触媒の有効利用が可能となる。また特別の加圧手段を設けることなく高圧の水素ガスが得られる。請求項 2 に係る発明は請求項 1 に係る発明であって図 1 に示すように、高圧の水素ガスを取出し、冷却した残液をそのまま或は濾過して、分散液に加える水素ガスの製造方法である。高圧の水素ガスを取出した残液は分散液の一部として再利用される。

【0005】請求項 3 に係る発明は図 4 に示すように、光反応性半導体金属板 49 とこれを担持する金属板 51 が貼り合わされた隔離板 52 で仕切られ半導体金属板 49 に面する第 1 室 53 と担持金属板 51 に面する第 2 室 54 にそれぞれ水 41 を供給する工程と、第 1 室 53 及び第 2 室 54 の水 41 をそれぞれ亜臨界状態又は超臨界状態にしかつ半導体金属板 49 に光を照射することにより第 1 室 53 の水 41 を酸素ガスに第 2 室 54 の水 41 を水素ガスにそれぞれ分解する工程と、第 2 室 54 で生じた亜臨界状態又は超臨界状態の水素ガスとを含む水 41 の圧力又は温度のいずれか一方又は双方を低下させることにより高圧の水素ガスを取出す工程とを含む水素ガスの製造方法である。光反応性半導体金属板 49 に光を照射すると、半導体金属板 49 上で水が分解して、



となり、第1室53に酸素ガスが発生する。また半導体金属板49に光を照射すると、担持金属板51上で水が分解して、



となり、第2室54に水素ガスが発生する。亜臨界状態又は超臨界状態の水は圧力が高いため、水の分子と担持金属板51との衝突頻度が増大し、水素生成効率が増大する。また特別の加圧手段を設けることなく高圧の水素ガスが得られる。請求項4に係る発明は請求項3に係る発明であって図4に示すように、高圧の水素ガスを取出した残液を冷却した後、この残液を第1室53及び第2室54に供給する水41に加える水素ガスの製造方法である。高圧の水素ガスを取出した残液は電解液の一部として再利用される。

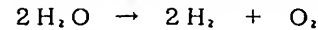
【0006】

【発明の実施の形態】本発明において、水の亜臨界状態とは200～374℃の温度でかつ160～215 kg/cm<sup>2</sup>の圧力にある水の状態を意味する。また水の超臨界状態とは374～400℃の温度でかつ215～300 kg/cm<sup>2</sup>の圧力にある水の状態を意味する。亜臨界状態における温度及び圧力の下限值未満では、反応が遅く、水の分解効率が良くない。また超臨界状態における温度及び圧力の上限値を超えると反応容器に負荷がかかり過ぎ、これも効率的でない。

【0007】本発明の請求項1及び2に係る水素ガスの製造方法を図1～図3に基づいて説明する。図1に示すように、水(H<sub>2</sub>O)11と光触媒の光反応性半導体粉末12を攪拌容器13に入れ攪拌して、水11に光反応性半導体粉末12を均一に分散した分散液(反応液)を調製する。光反応性半導体粉末12は酸化チタン、酸化亜鉛、酸化タングステン、酸化セリウム等の金属酸化物やRb-Nb、Pb-Nb系の複合金属酸化物等がジルコニウム、白金、ニッケル等の金属上に担持された構造の粒径が10～500 μmの微粒子である。上記分散液はバルブ14を介して水槽16に供給される。この水槽16に貯えられた分散液はバルブ17を介してポンプ18で加圧され、かつプレヒータ19で加熱されて亜臨界状態又は超臨界状態となって反応容器21に圧送される。反応容器21には図1の矢印で示す照射光を透過させるサファイア、ダイヤモンド等の材料からなる窓22が形成されている。照射光としては波長300 nm以下の紫外線が好ましいが、これ以上の波長を有する光でも使用することができる。こうした光照射源としては水銀ランプ、ハロゲンランプ等が使用される。反応容器21の上下両面には反応容器21を加熱するヒータ23が設けられ、これにより反応容器21内において分散液は亜臨界状態又は超臨界状態を維持する。

【0008】この状態において光を窓22から反応容器21内の分散液に照射すると、光は光触媒の光反応性半導体粉末12の表面において水分子を分解し、次式で示

すように水素ガス及び酸素ガスを生じる。



反応容器21で発生した水素ガス及び酸素ガスを含む分散液は反応容器21から取出され、ヒータ24で所定温度に加熱された後、脱酸素槽26に送られる。図2に示すように、脱酸素槽26の内壁には酸素と反応するチタン等の金属の板27が分散液と十分な接触面積を確保できるように数多く所定間隔を保って配置されており、その結果、分散液が脱酸素槽26内を通過する間に金属板27と酸素が反応して分散液中の酸素が除去される。酸素を除去されて水素ガスを含む分散液は脱酸素槽26から取出され、バルブ28を介して水素と水の分離槽29へ送られて圧力を降下することにより水と高圧の水素ガスに分離される。

【0009】分離された高圧の水素ガスはバルブ31を介して高圧水素貯蔵槽32に送られて保存される。水素と水の分離槽29で高圧の水素ガスを分散液から取出した残液は冷却器33で冷却された後、フィルタ34に送られる。残液中に含まれる光反応性半導体粉末12は上述のように酸化チタン等の金属酸化物をジルコニウム、白金等の金属上に担持させた構造の微粒子であるため、反応容器21内で光触媒として使用された後においては、例えば担持金属の白金と金属酸化物の酸化チタンとが分離して光触媒としての機能を喪失する場合がある。このような場合には、分離した担持金属と金属酸化物を上記フィルタ34で濾過して取り除く。フィルタ34を通過した残液はポンプ36で加圧されて水槽16に回収され、反応容器21へ送られる分散液の一部として再利用される。光反応性半導体粉末12が光触媒としての機能を喪失していない場合には、水素と水の分離槽29で高圧の水素ガスを分散液から取出した残液は冷却器33で冷却された後、フィルタ34に送らないで直接にポンプ36に送られ加圧されて水槽16に回収され、反応容器21へ送られる分散液の一部として再利用される。

【0010】図1及び図2に基づく実施態様では脱酸素槽26は反応容器21の外側に独立して設けられる。しかしこれ以外にも脱酸素槽26を反応容器21の内側に反応容器21と一体に設けることも可能である。例えば図3に示すように、反応容器21内の出口部分に脱酸素装置37を設けて、反応容器21内で生じた酸素を除去してもよい。即ち、脱酸素装置37の内壁には酸素と反応する金属板38が分散液と十分な接触面積を確保できるように数多く所定間隔を保って配置されており、反応容器21で発生した水素ガス及び酸素ガスを含む分散液が矢印で示すように脱酸素装置37内を通過する間に金属板38と酸素が反応して分散液中の酸素が除去される。この金属板38の材質としてはチタン等が挙げられる。酸素を除去されて水素ガスを含む分散液は脱酸素装置37の出口から矢印で示すように取出され、バルブ28を介して水素と水の分離槽29へ送られる。

【0011】本発明の請求項3及び4に係る水素ガスの製造方法を図4に基づいて説明する。図4に示すように、水(H<sub>2</sub>O)41をバルブ42を介して水槽43に供給する。水槽43に貯えられた水41はバルブ44を介してポンプ46で加圧され、かつプレヒータ47で加熱されて亜臨界状態又は超臨界状態となって反応容器48に圧送される。反応容器48は光反応性半導体金属板49とこれを担持する金属板51が貼り合わされた隔離板52で仕切られる。その結果、光反応性半導体金属板49に面する第1室53と上記担持金属板51に面する第2室54が形成される。光反応性半導体金属板49の材料としてはチタン、SrTiO<sub>3</sub>、BaTiO<sub>3</sub>などのTi化合物やNb系の化合物等の半導体金属が挙げられる。また担持金属板51の材料としては白金、ジルコニウム、ニッケル、ロジウム等の金属が挙げられる。亜臨界状態又は超臨界状態となって反応容器48に圧送された水41は反応容器48の第1室53と第2室54にそれぞれ供給される。反応容器48の上下両面には反応容器48を加熱するヒータ56が設けられ、これにより反応容器48の第1室53及び第2室54内において水は亜臨界状態又は超臨界状態を維持する。反応容器48にはサファイア、ダイヤモンド等の材料からなる窓57が形成されている。

【0012】この状態において、照射光として例えば、波長300nm以下の紫外線を窓57から光反応性半導体金属板49の表面に照射すると、光は半導体金属板49の表面において水分子を分解して第1室53に酸素ガスが発生し、第2室54に水素ガスが発生する。第1室53と第2室54は隔離板52で仕切られているため、発生した酸素ガスと水素ガスが混じり合うことはない。第2室54で発生した水素ガスを含む水は第2室54から取出され、減圧弁58を介して水素と水の分離槽59へ送られて圧力を低下することにより水と高圧の水素ガスに分離される。分離された高圧の水素ガスはバルブ61を介して高圧水素貯蔵槽62に送られて保存される。水素と水の分離槽59で水素ガスから分離された水は冷却器63で冷却された後、ポンプ64で加圧されて水槽43に回収され、反応容器48へ送られる水の一部として再利用される。第1室53で発生した酸素ガスを含む水は第1室53から取出され、酸素と水の分離槽66へ送られて圧力を低下することにより水と酸素ガスに分離される。分離された酸素ガスはバルブ67を介して高圧酸素貯蔵槽68に送られて保存される。酸素と水の分離槽66で酸素ガスから分離された水は冷却器69で冷却された後、水槽43に回収され、反応容器48へ送られる水の一部として再利用される。

【0013】

【発明の効果】以上述べたように、本発明によれば、水に光反応性半導体粉末を均一に分散した分散液を作り、この分散液を亜臨界状態又は超臨界状態にし光を照射して水を水素ガスと酸素ガスに分解し、水素ガスと酸素ガスに分解した亜臨界状態又は超臨界状態の光反応性半導体粉末を含む水から酸素ガスを取除き、酸素ガスを取除いた亜臨界状態又は超臨界状態の残部の圧力又は温度のいずれか一方又は双方を低下させることにより高圧の水素ガスを取り出すようにしたので、触媒として作用する光反応性半導体粉末の表面で発生した水素ガスは速やかに水と均一相を形成し、触媒表面への水素ガスの吸着は少なくなり水素生成効率が增大する。また触媒が反応液中に溶解して喪失する光溶解の現象が極めて起こり難く、触媒の有効利用が可能となる。

【0014】また本発明によれば、光反応性半導体金属板とこれを担持する金属板が貼り合わされた隔離板で仕切られ、半導体金属板に面する第1室と担持金属板に面する第2室にそれぞれ水を供給し、第1室及び第2室の水をそれぞれ亜臨界状態又は超臨界状態にしかつ光反応性半導体金属板に光を照射することにより第1室の水を酸素ガスに第2室の水を水素ガスにそれぞれ分解し、第2室で生じた亜臨界状態又は超臨界状態の水素ガスを含む水の圧力又は温度のいずれか一方又は双方を低下させることにより高圧の水素ガスを取り出すようにしたので、水の分子と担持金属板との衝突頻度が増大し、水素生成効率が增大する。更に特別の加圧手段を設けることなく高圧の水素ガスが得られる。

【図面の簡単な説明】

【図1】本発明の水素ガスの製造装置の構成図。

【図2】図1の装置で脱酸素槽の構造を説明する構成図。

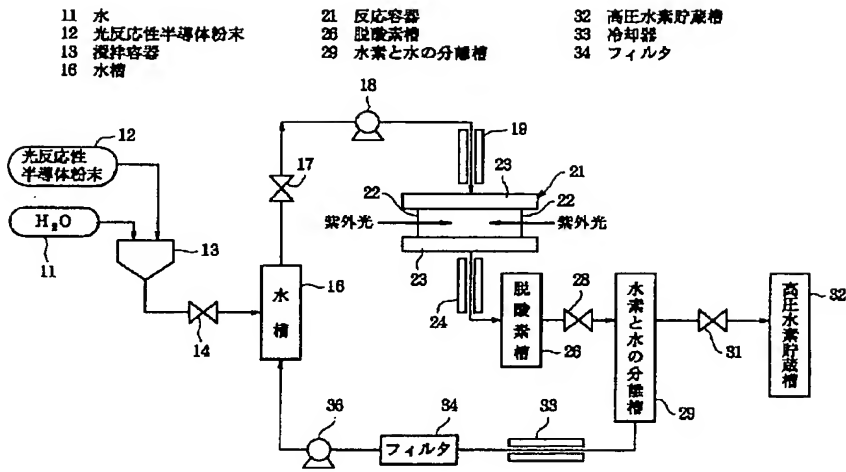
【図3】脱酸素装置を反応容器の内部に設けた実施態様を示す構成図。

【図4】本発明の水素ガスの製造装置の別の実施態様を示す構成図。

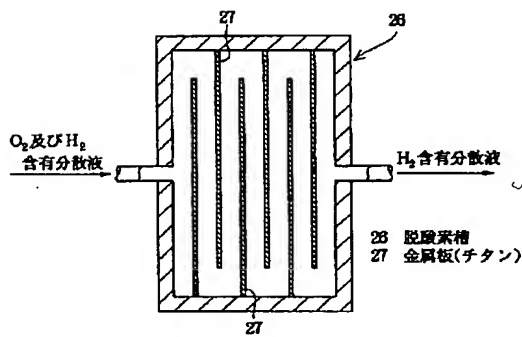
【符号の説明】

- 11, 41 水
- 12 光反応性半導体粉末
- 16, 43 水槽
- 21, 48 反応容器
- 26 脱酸素槽
- 29, 59 水素と水の分離槽
- 32, 62 高圧水素貯蔵槽
- 49 光反応性半導体金属板
- 51 金属板
- 66 酸素と水の分離槽
- 68 高圧酸素貯蔵槽

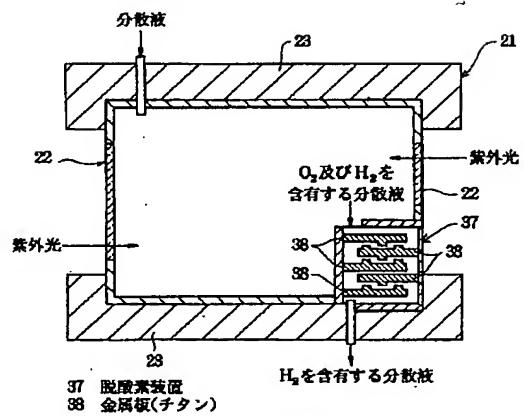
【図1】



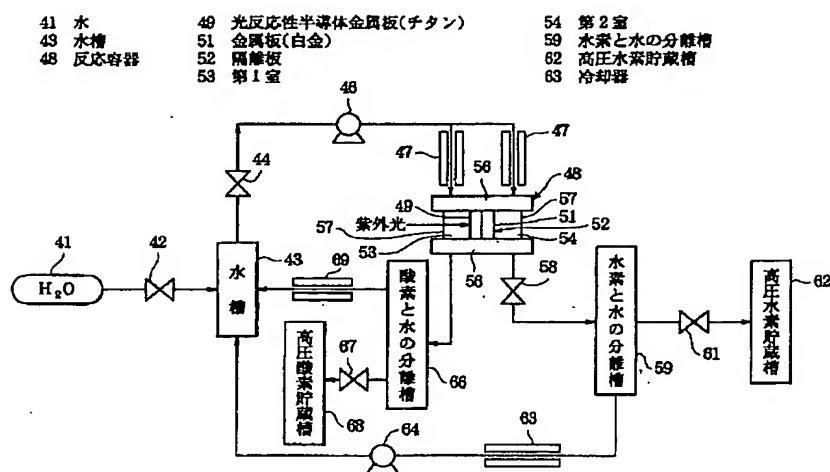
【図2】



【図3】



【図4】



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